



Desulphurization Techniques for Liquid Fuel A Review

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ABSTRACT

This review paper discusses the different advanced process for desulphurization of liquid fuel such as Adsorptive desulphurization, Extractive desulphurization, Oxidative desulphurization, Hydro desulphurization, Biodesulphurization, Desulphurization by ionic liquids, for obtaining sulphur free or low sulphur fuel and their recent advances in research field. In this review, The effect of desulphurization on liquid fuel under different conditions is also investigated.

Keywords

Sulphur, Desulphurization, Liquid fuel, Adsorptive desulphurization, Extractive desulphurization, Oxidative desulphurization, Hydrodesulphurization, Biodesulphurization, ionic liquids

I. INTRODUCTION

Desulphurization methods mainly cover hydrodesulphurization, oxidative desulphurization and adsorptive desulphurization in order to realize the desulphurization process the key is how to select proper adsorbents which cover molecular sieves, activated carbon, ion exchange resin and activated carbon fibres. (Cao Zhitao et al. 2011) The topic of research deals with desulphurization of liquid fuel concerned with different methods removal of sulphur compounds present in crude petroleum and a product manufactured from crude. The requirement of ultraclean transportation fuels particularly gasoline diesel and jet fuels has resulted in continuing worldwide effort to dramatically reduce the sulphur levels in them (Dezhi et al 2012). The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rain and air pollution, deforestation, smog and global warming (Adeyi et al. 2012). Therefore there is need to research on new desulphurization methods which are cost effective, more efficient and meet the environmental regulations and refining requirements. There are different types of techniques that can reduce or remove sulphur compounds such as adsorptive desulphurization, Extractive desulphurization, Hydrodesulphurization, Biodesulphurization.

II. DESULPHURIZATION METHODS

A. Adsorptive desulfurization



Adsorption can be used for desulfurization of petroleum fractions based on the ability of solid adsorbent material to selectively adsorb organic sulfur compounds. There are two types of adsorptive desulfurization: adsorptive desulfurization during which physical and/or chemical adsorption of organic sulfur compounds takes place on the surface of the adsorbent, and reactive adsorption desulfurization during which organic sulfur compounds react with chemical species on the surface of the adsorbent and the sulfur is chemically bound, usually in the form of sulfide, while the newly-formed hydrocarbon compound is released into the stream. [1]Bhattacharyulu et.al [2] have studied desulphurization of hydrocarbon liquid fuels by adsorption. The investigators used batch reactor for sorption of sulfur onto activated carbons which prepared from black liquor and Phosphoric acid and nitrogen reactor used as intercalating agents. Authors also reported that intra- particle diffusion resistance has been overcome due to stirring and experimental data obtained obeys Langmuir adsorption isotherm model. Shimizu, et al [3] used rice husk activated carbon for adsorptive removal of sulphur compounds. The adsorption is conducted using rice husks carbonized in N₂ at 400°C for 1 h and then activated in CO₂ at 850°C for 1 h. Isam and Zubaid et al [4] used Adsorption desulfurization of diesel oil studied using seven sorbents such as Bentonite, acid activated bentonite, date palm kernel powder, acid activated date palm kernel powder, sawdust powder, and commercial powder and granules activated carbon. The study conducted the experiments using amount of sorbents was ranging from 0-5% by mass in a batch process at room temperature with contact time of two hours. Liquid phase adsorptive desulphurization of diesel fuel studied by Karagianakis [5]. The studies were conducted for the lab-scale liquid desulfurization of commercial diesel fuel via adsorption, under ambient conditions, employing a high- surface area activated carbon (AC) sorbent. Arturo et.al [6] studied desulfurization of a commercial diesel fuel by different adsorbents in a fixed bed adsorber operated at ambient temperature and pressure. Investigators reported that the best adsorbent, AC/Cu(I)-Y (layered bed of 15 wt % activated carbon followed by Cu(I)Y), is capable of producing 30 cm³ of diesel fuel per gram of adsorbent with a weighted average content of 0.15 ppmw-S, and about 20 cm³ of diesel fuel per gram of adsorbent with a weighted average content of 0.06 ppmw-S.

B. Extractive desulfurization

Extraction can be used for desulfurization because of higher solubility of organic sulfur compounds in appropriate solvent than other hydrocarbons present in a petroleum fraction. The organic sulfur compounds are removed from the feed into the solvent, after which the mixture of sulfur rich solvent and feed is separated. [1] CHU Xuemei [7] et.al have studied Desulfurization of Diesel Fuel by Extraction with [BF₄]⁻ based Ionic Liquids. Authors have systematically investigated the extractive removal of sulfur compounds from Dongying and Liaohe diesel fuels with [BF₄]⁻ based ionic liquids. T. Adami et al [8]. reported the Extractive desulfurization of FCC gasoline with two solvents (sulfolane and furfural). Authors carried out different experiments for determination of suitable



solvent regarding the process parameters including temperature, batch time, solvent / FCC gasoline ratio and extraction times. They investigate that maximum desulfurization efficiency is obtained at high levels of temperature and sulfolane / FCC gasoline ratio; time in researched range of values had small impact and minimum sulfur content in raffinate of 196 mg kg⁻¹ was obtained at higher levels of temperature, time and sulfolane / FCC gasoline ratio. Authors also developed mathematical model for predicting sulfur content in raffinate after extractive batch process with sulfolane and proven with analysis of variance. Wang Haojie et.al.[9] Deep Extractive Desulfurization of Gasoline with Ionic Liquids Based on Metal Halide Ionic liquid. Different desulfurization activity of ionic liquid is tested by authors. Investigators also reported that FCC gasoline could be obtained after three extraction runs at an ionic liquid/oil volume ratio of 0.1, with the yield of FCC gasoline reaching 94.3%. And the ionic liquid could be recycled 5 times with merely a slight decrease in activity. Desulfurization of Liquid Fuels by Selective Extraction Method studied by K.Abinaya.[10] Author investigates various new approaches for desulfurization of ultra clean gasoline, diesel and other liquid fuels by extraction with ionic liquids. And investigator also investigates extraction method deep sulphur reduction by using various ionic liquid.

C. Oxidative desulfurization

Oxidative desulfurization is a process during which organic sulfur compounds are oxidized and subsequently removed from the feed by a separation method. The methods used for separating oxidized sulfur compounds from treated fuel feeds include extraction, adsorption, distillation, and thermal decomposition.[1] Research advances in oxidative desulfurization technologies for the production of low sulphur fuel oils studied by Gaofei Zhang and Wang [11]. Authors reviewed research progress in the oxidative desulfurization (ODS) technology. JIANG [12] developed a new alternative oxidative desulfurization process using emulsion catalysts, in which amphiphilic emulsion catalysts can selectively oxidize the sulfur-containing molecules present in diesel to their corresponding sulfones when using H₂O₂ as the oxidant under mild conditions. Authors studied oxidative desulfurization of fuel oils, such as using H₂O₂/organic acids, H₂O₂/heteropolyacid, H₂O₂/Ti-containing zeolites, and other non-hydrogen peroxide systems (e.g., t-butyl hydroperoxide etc.) Investigators also reported that sulphur level of a pre hydro treated diesel can be lowered from a few hundred 3g/g to 0.1 3g/g after oxidation and subsequent extraction whereas the sulfur level of a straight-run diesel can be decreased from 6000 to 30 3g/g after oxidation and extraction. Gaofei Zhang et.al[13] have studied Advances in oxidative desulfurization technologies for the production of low sulphur fuel. Authors use oxidative desulfurization (ODS) technology for the removal of fuel oils. Authors also investigate different methods, such as according to the oxidants involved H₂O₂ oxidation method, organic oxidant method, photochemical oxidation method, as well as those involving the use of plasma or ultrasound. CHEN Lanju et.al[14] have studied Oxidative Desulfurization of Simulated Gasoline over Metal Oxide-loaded Molecular Sieve. Authors



conducted a experiment for oxidative desulfurization in the hydrogen peroxide (H_2O_2) and formic acid oxidative system over metal oxide-loaded molecular sieve and sulfur compounds of thiophene (C_4H_4S) and 3-methylthiophene (3-MC $_4H_4S$) dissolved in n-heptane are used for testing. and they investigates the effects of the oxidative system, loaded metal oxides, phase transfer catalyst, the addition of olefin and aromatics on sulfur removal. Authors also investigated that the sulfur removal rate of simulated gasoline in the H_2O_2 / formic acid sys- tem was higher than in other oxidative systems. Serhiy Pysh'yev et.al[15] have studied Application of non catalytic oxidative desulphurization process for obtaining diesel fuels with improved lubricity. Authors carried out experiment for desulphurization of diesel oil air oxidation without the catalysts in the presence of water. Authors used joint adsorption and rectification for extraction of sulphuric compounds oxidation and analyse samples of desulphurized diesel fuel. CHEN Lanju et.al[16] reported an Oxidative Desulfurization of Simulated Gasoline over Metal Oxide-loaded Molecular Sieve. Authors have conducted experiments for testing of a gasoline consisting sulfur compounds of thiophene and 3-methylthiophene dissolved in n-heptane for the oxidative desulfurization in the hydrogen peroxide (H_2O_2) and formic acid oxidative system over metal oxide-loaded molecular sieve. They investigates in detail effect of different factors such as Oxidative system, loaded metal oxides, phase transfer catalyst, the addition of olefin and aromatics .Investigators are also investigates that the sulfur removal rates of C_4H_4S and 3-MC $_4H_4S$ are enhanced when phase transfer catalyst (PTC) was added. Dishun Zhao et.al [17] have studied Oxidative Desulfurization of Fuel Oil by Pyridinium Based Ionic Liquids. Authors have conducted experiments for preparation of N-butyl pyridinium based ionic liquid [BPy] BF $_4$.and they investigates the effect of extraction desulfurization on model oil with thiophene and dibenzothiophene .on the basis of experimental results ,authors concluded that the ionic liquid [BPy]BF $_4$ has a better desulfurization effect at the conditions $V(IL)/V(Oil) /V(H_2O_2) = 1:1:0.4$, temperature 55 °C, the time 30 min.

D. Hydrodesulfurization processes

Hydrodesulfurization (HDS), a mild form of hydro cracking, is a refining process used for removing organic sulfur compounds from petroleum fractions. Zhonghuo Deng et.al [18] have studied hydrodesulfurization of diesel in a slurry reactor .Investigators carried out experiments for hydrodesulphurization of diesel using catalyst NiMoS/ Al_2O_3 in a high-pressure autoclave at operating conditions 4.8–23.1wt% catalyst in the reactor, 320–360°C, 3–5MPa pressure, and 0.56–2.77L/min hydrogen flow rate. Authors have reported that the reaction rate was proportional to the catalyst amount and increased with temperature, pressure and hydrogen flow rate. Herna et al., [19] studied hydrodesulphurization process for removal of sulphur from liquid fuel using Co-Mo/ Al_2O_3 or Ni-Mo/ Al_2O_3 catalyst. Authors also reported that the reactor size needs to be increased by factors of 5-15.4 .Investigators showed that aqueous- phase copper(II)-exchanged Y-zeolites, when auto



reduced to Cu(I)-Y, are capable of removing 0.20 mol of organo-sulfur species from a commercial diesel fuel (297.2 ppmw total sulfur) per gram of zeolite5-7 .

E. Biodesulphurization

Biodesulphurization is a process that removes organic sulfur compounds from fossil fuels using enzyme-catalyzed reactions. Biocatalytic sulfur removal from fuels has applicability for producing low sulfur gasoline and diesel fuels.[1] Aribike et.al[20] have studied Microbial Desulfurization of Diesel by *Desulfobacterium anilini*. Authors have studied use of *Desulfobacterium anilini* isolated from petroleum products-polluted soil and the removal of sulphur containing hydrocarbons from diesel. Investigators carried out experiments 300⁰C and normal atmospheric pressure and concluded that the peaks of benzothiophene and dibenzothiophene in diesel significantly decreased after biodesulphurization, using Gas chromatography analysis with a pulsed flame photoatomic detector .Authors also reported that at the end of 72 hours, organism desulfurized 82% of the analyzed sulfur in diesel.Adegunlola et.al[21] reported Microbial desulphurization of crude oil using *Aspergillus flavus* .Authors carried out experiment for removal of sulphur from crude oil using sodium metabisulphite whose concentration is increase by culturing immobilized spores of *Aspergillus flavus*. Investigators investigated that 10g, 50g and 100g of immobilized spores of *A. flavus* remove 49.6%, 94.7% and 53.9% sulphur respectively when added to 100ml the crude oil for seven days. Toshiki Furuya et.al[22] have studied thermophilic biodesulphurization of hydrodesulfurized light gas oils by *Mycobacterium phlei*. Investigators carried out experiment for biodesulphurization for reduction of 60 to 70 % sulphur content from hydrodesulfurized LGOs. Authors have concluded that when cells were incubated at 45⁰C with hydrodesulfurized LGOs in the reaction mixtures containing 50% (v/v) oils, biodesulphurization reduced the sulfur content from 390 to 100 ppm S (B-LGO), from 120 to 42 ppm S (F-LGO) and from 34 to 15 ppm S (X-LGO).S.Labana et.al[23] Studied Desulphurization of dibenzothiophene and diesel oils by bacteria. Investigators used gas chromatography (GC) and GC-mass spectrometry for the desulphurization of DBT by bacteria. Authors have reported that sulphur contents of culture supernatants of *Rhodococcus sp.* and *A. sulfureus* grown with DBT are analysed by X-ray fluorescence indicating sulphur levels of 8 and 10 ppm .BAN Lili et al[24] have studied Deep Desulfurization of Diesel Fuels with Plasma/Air as Oxidizing Medium, Diperiodatocuprate (III) as Catalyzer and Ionic Liquid as Extraction Solvent. Authors have used oxidative desulfurization of oil using by dielectric barrier discharge (DBD) plasma in the presence of air plus and extraction with the oxidation-treated fuel put over ionic liquid [BMIM]FeCl₄ (1-butyl-3-methylimidazolium tetrachloro ferrate).Authors have also reported that high desulfurization rate is obtained during oxidation of benzothiophene (BT) or 4,6-DMDBT (4,6-dimethyl-dibenzothiophene) .S. Abbad et.al[26] have studied Microbial Desulfurization of Diesel Oils by Selected Bacterial Strains. Authors studied ultra deep desulfurization of diesel oils by using microbial strains. Investigators reported that 15 pure strains able to use DBT as a sole sulfur source



and to convert it to 2-hydroxybiphenyl (HBP) were obtained from different soils. and 5 isolates belonging to the Rhodococcus/Gordonia cluster and exhibiting .

III.CONCLUSION

The purpose of this study is to review different desulphurization techniques. This paper review various paper publishes in different journals on desulphurization process in different ways such as adsorptive desulphurization, Extractive desulphurization, Hydrodesulphurization, Biodesulphurization for sulphur removal for an industrial scale reactor.

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